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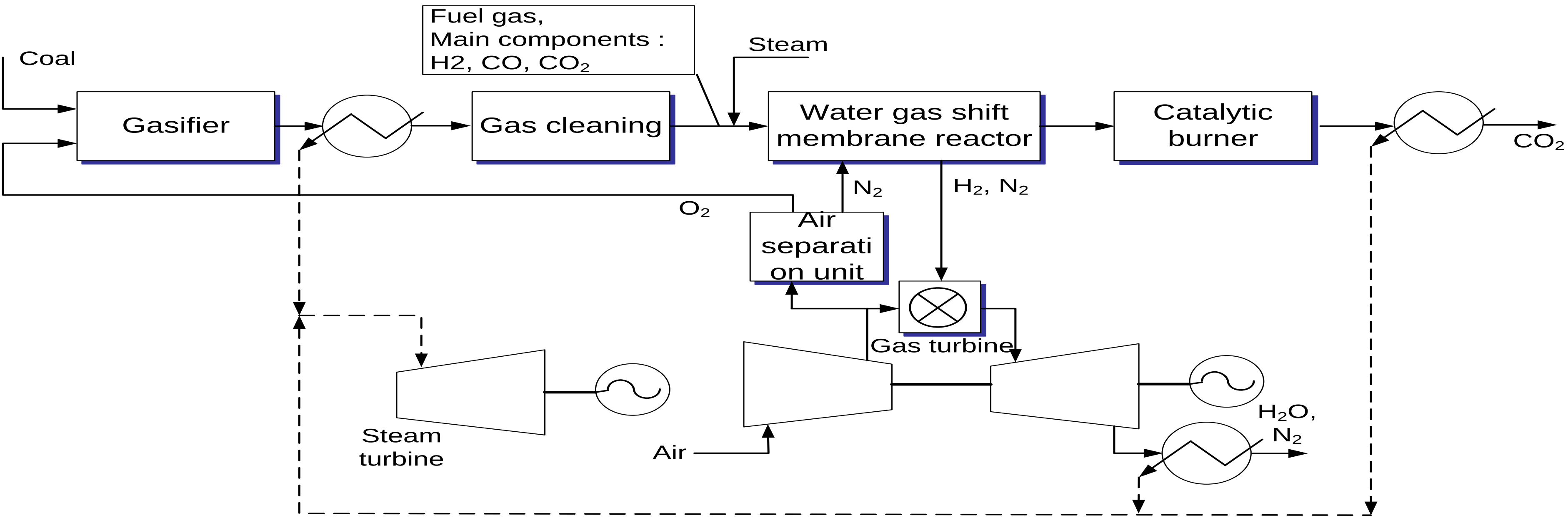
DE-FE0001322 Hydrogen Selective Exfoliated Zeolite Membranes

Proposal in response to Funding Opportunity NO. DE-PS26-08NT00699-01

Pre-combustion carbon capture technologies for coal-based gasification plants

Topic Area 1 – High-Temperature, High-Pressure Membranes

Hydrogen Selective Membranes in IGCC Plants

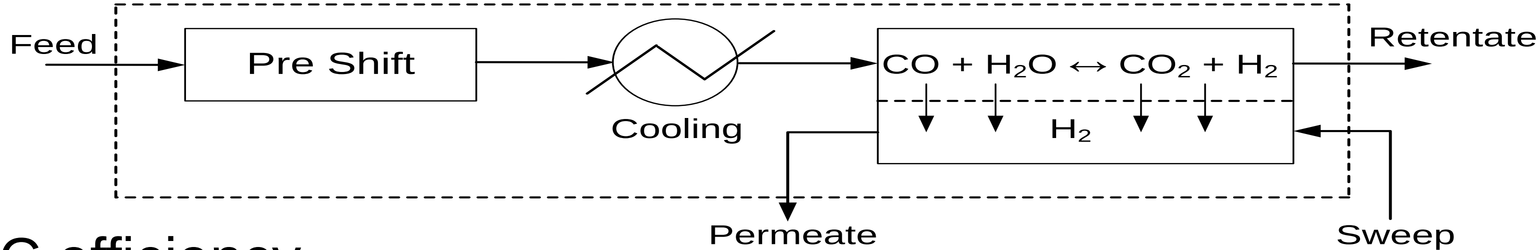


Challenges under WGS conditions of IGCC plants

- high temperature and pressure
- presence of impurities (H_2S)

Bracht et al., **Energy Convers.Mgmt** 38, S159-164 (1997)

IGCC w/ WGS MR



IGCC efficiency

- without CO_2 capture: 46.7%
- with conventional CO_2 removal: 40.5%

With WGS MR and CO_2 recovery: 42.8% based on

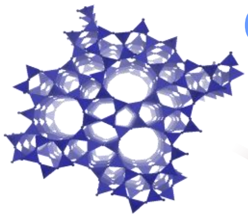
- 35 atm feed, 20 atm permeate (15 atm pressure drop)
- 330^oC in the feed
- hydrogen/carbon dioxide selectivity = 15
- hydrogen permeability = 0.2 mol/(m^2.s.bar)

Membrane Area Needed: 2,200 m^2 (400MW)

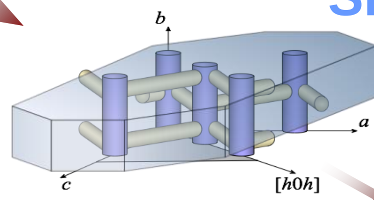
Bracht et al., **Energy Convers.Mgmt** 38, S159-164 (1997)

Motivation: Hierarchical Manufacturing of Zeolite Films

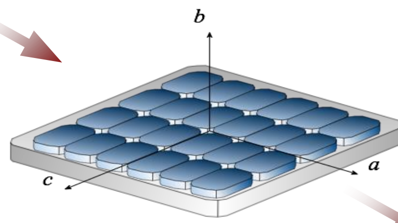
For a Review:
Mark A. Snyder, Michael Tsapatsis,
Angew. Chem. Int. Ed. **2007**, *46*, 7560–7573



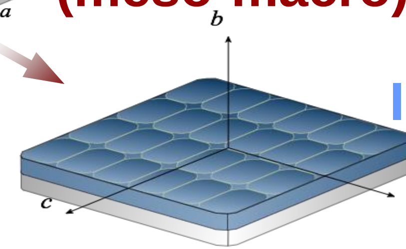
Crystal Structure (nm)



Shaped Crystal (10-100nm)



Oriented Monolayer of Crystals (meso-macro)



Intergrown Film

AIChE Journal, 42(11), 3020-3029 (1996)

Chemistry of Materials 10, 2497-2504 (1998)

Science 300:(5618), 456-460 (2003)

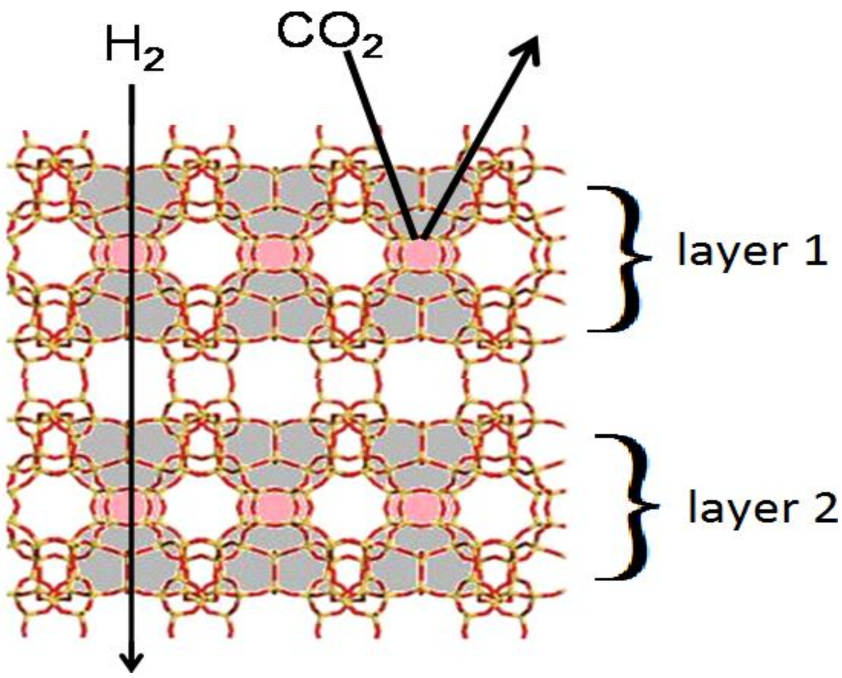
Angew. Chem. Int. Ed. 45, 1154-1158 (2006)

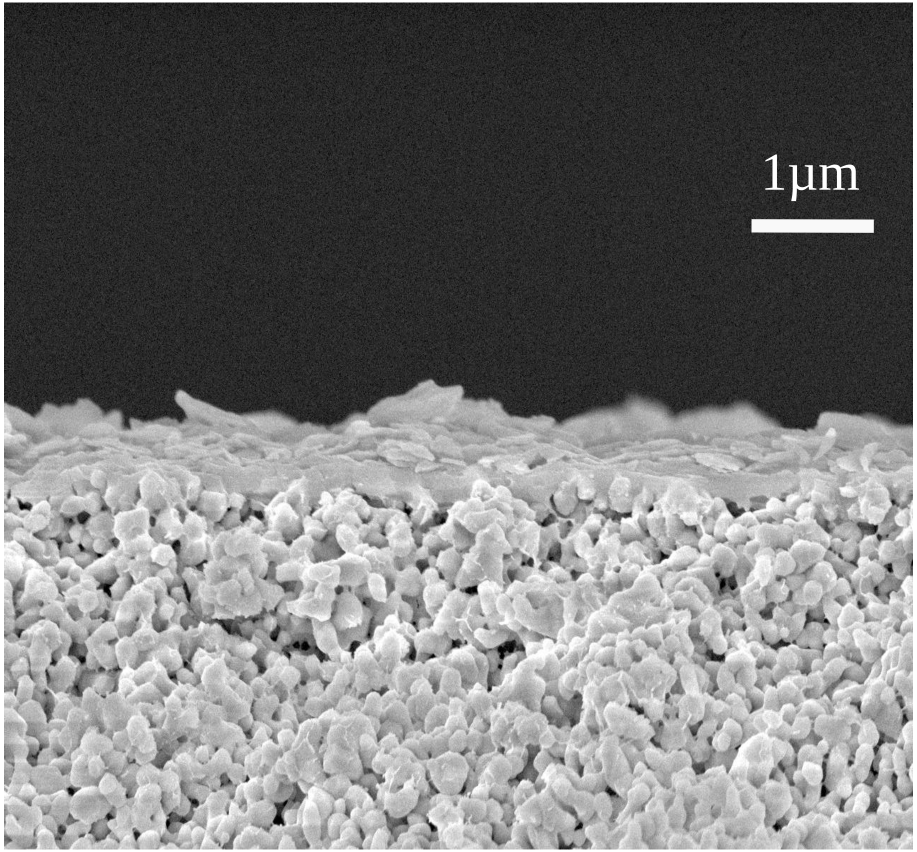
Nature Materials, 7(12), 984-991(2008)

Science 325 (5940), 590-594 (2009)

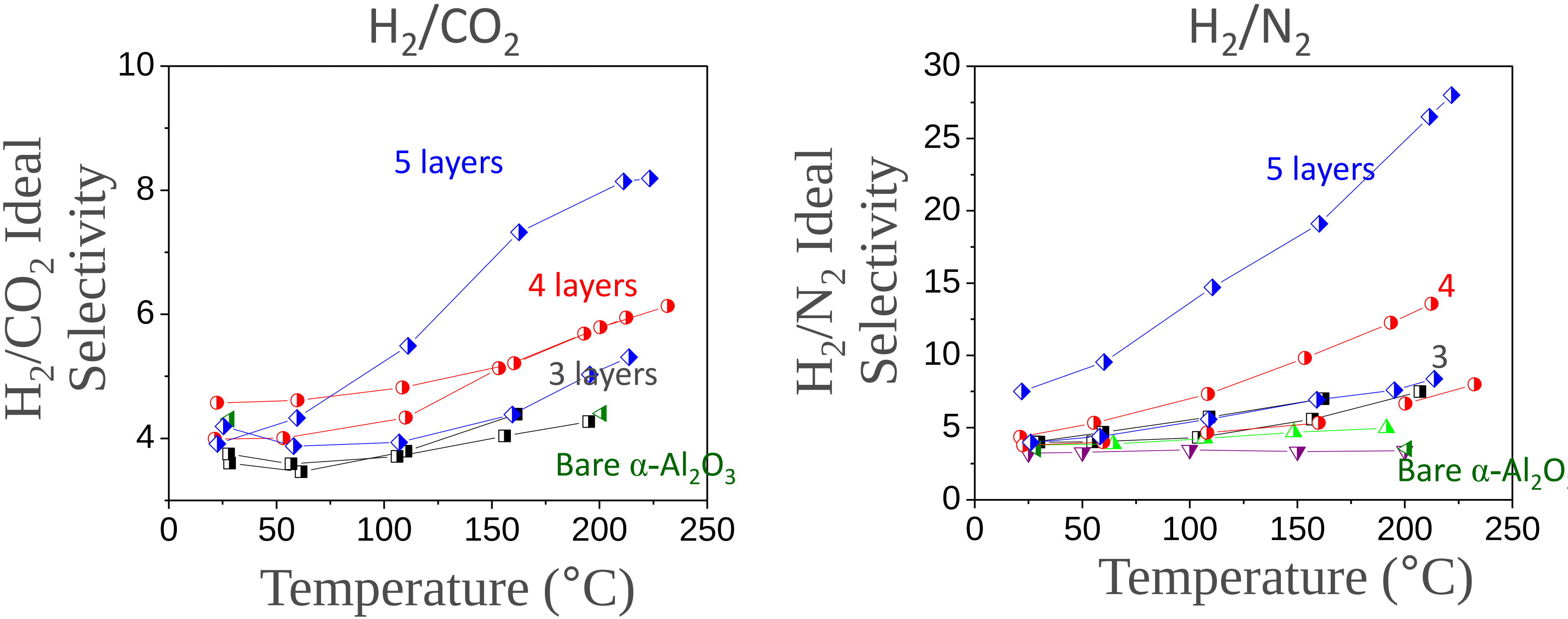
Layer by Layer Deposition (JACS 132(2), 448-449 (2010))

5 layers of MCM-22/surfactant-templated-mesoporous-silica on porous alumina



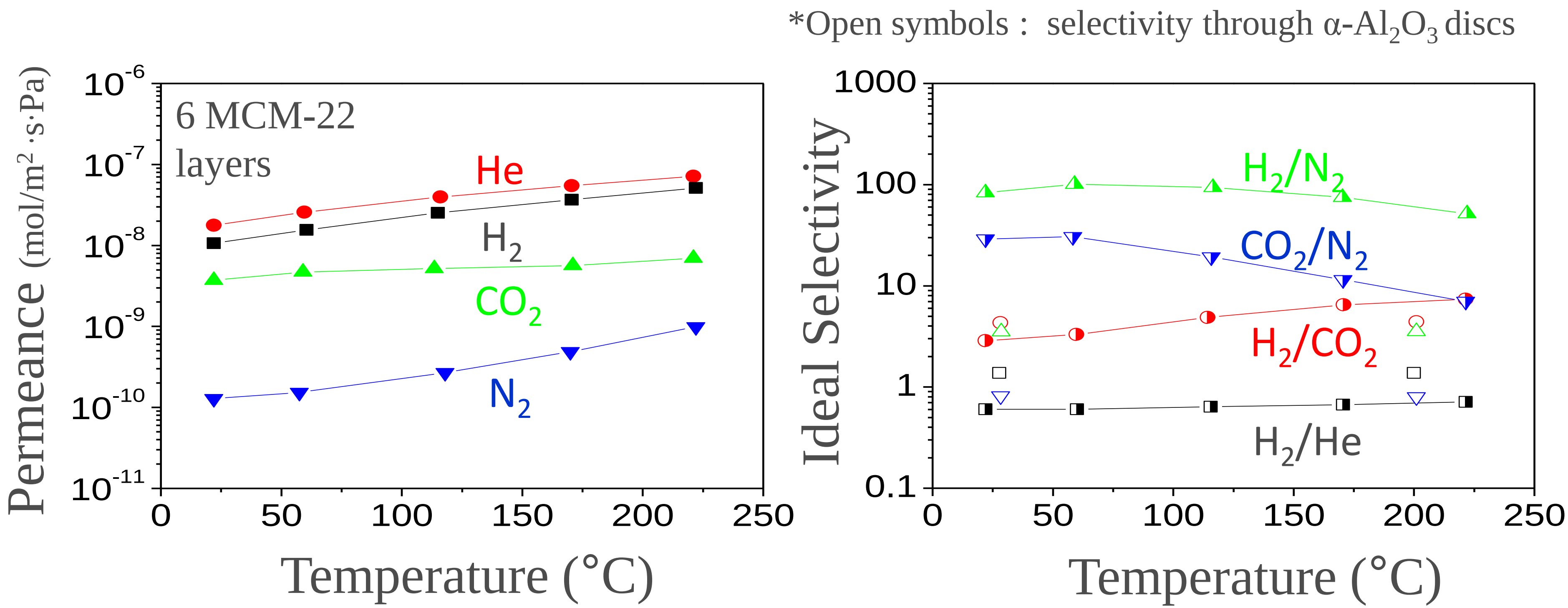


Comparison of Ideal Selectivity



The ideal selectivity (H_2/CO_2 and H_2/N_2) increased monotonically with temperature and improved with the number of deposition cycles.

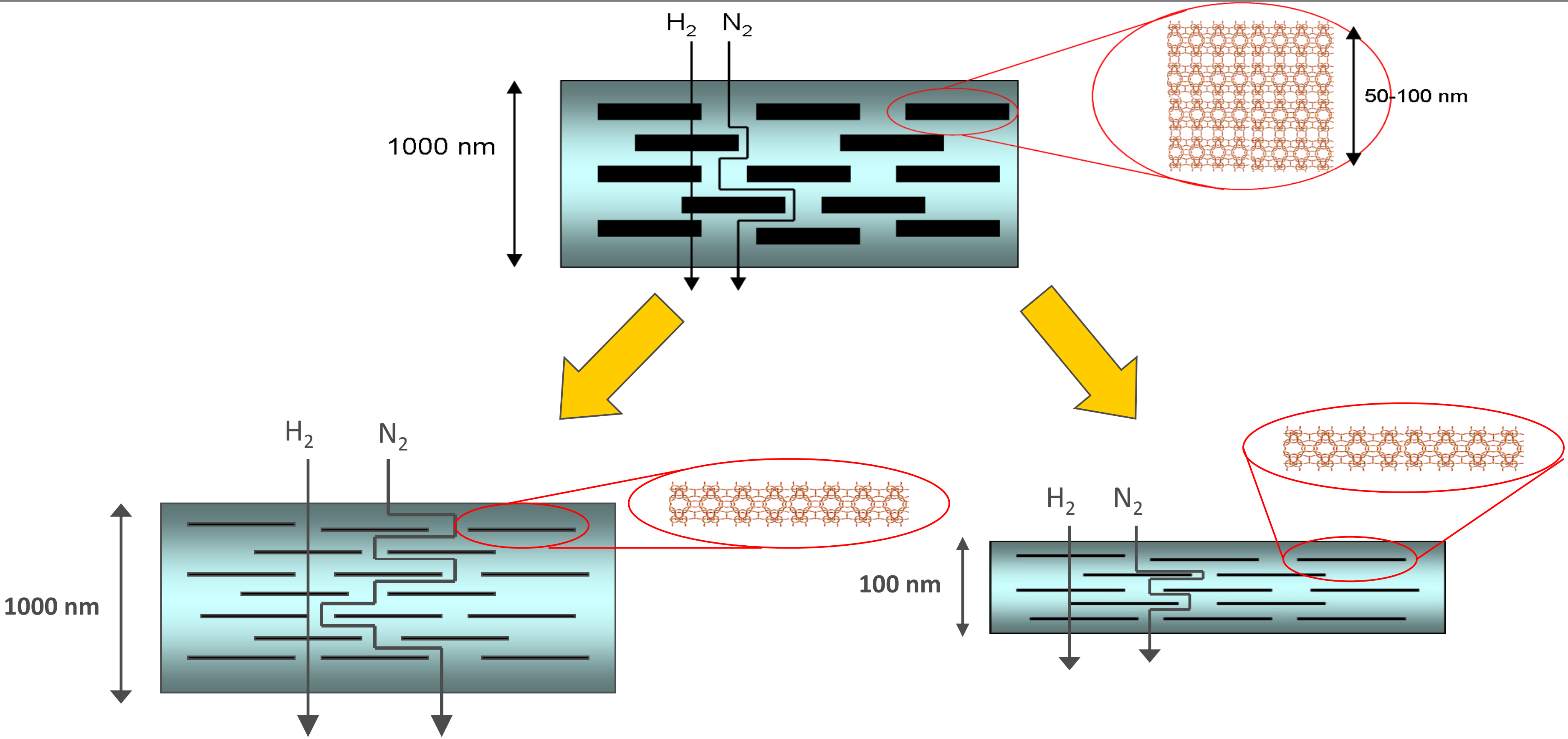
MCM-22/Silica Membranes for Hydrogen Separations



Choi J. and Tsapatsis M. **Journal of the American Chemical Society** 132(2), 448-449 (2010)

Experimental Demonstration of Selective Flake Composite Concept

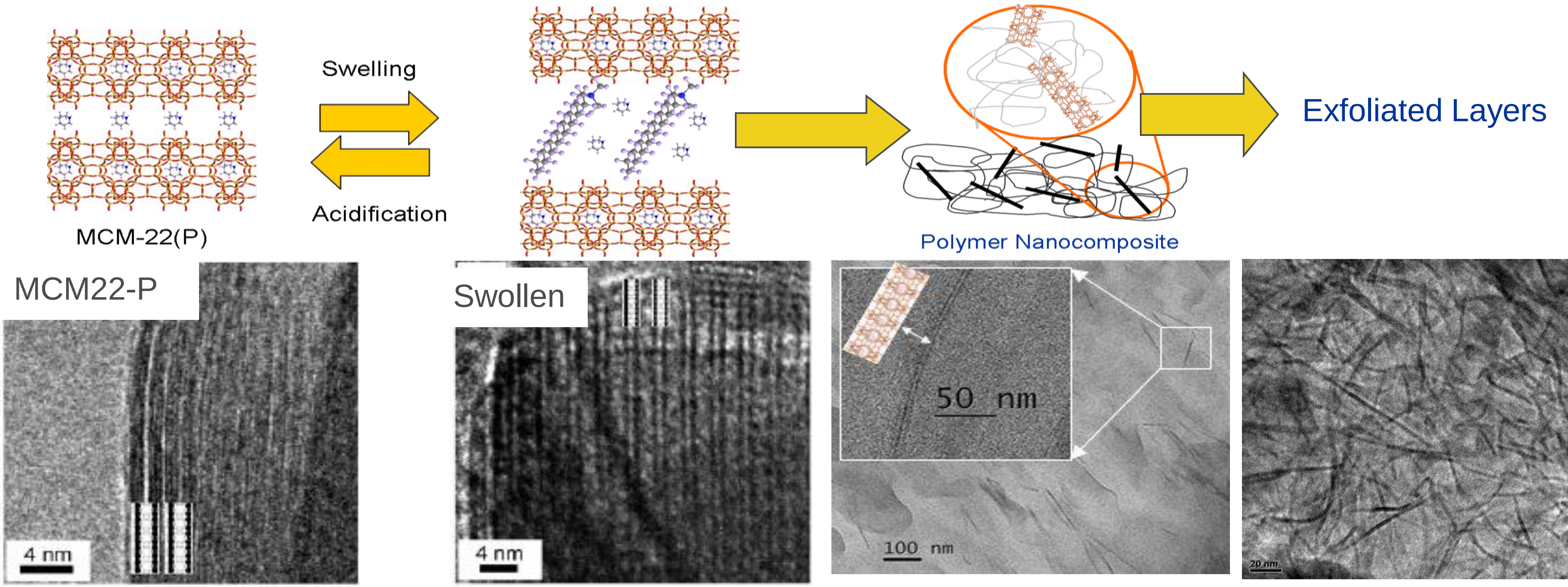
Advantages by Reduction in Flake Thickness



Increase selectivity without decreasing throughput

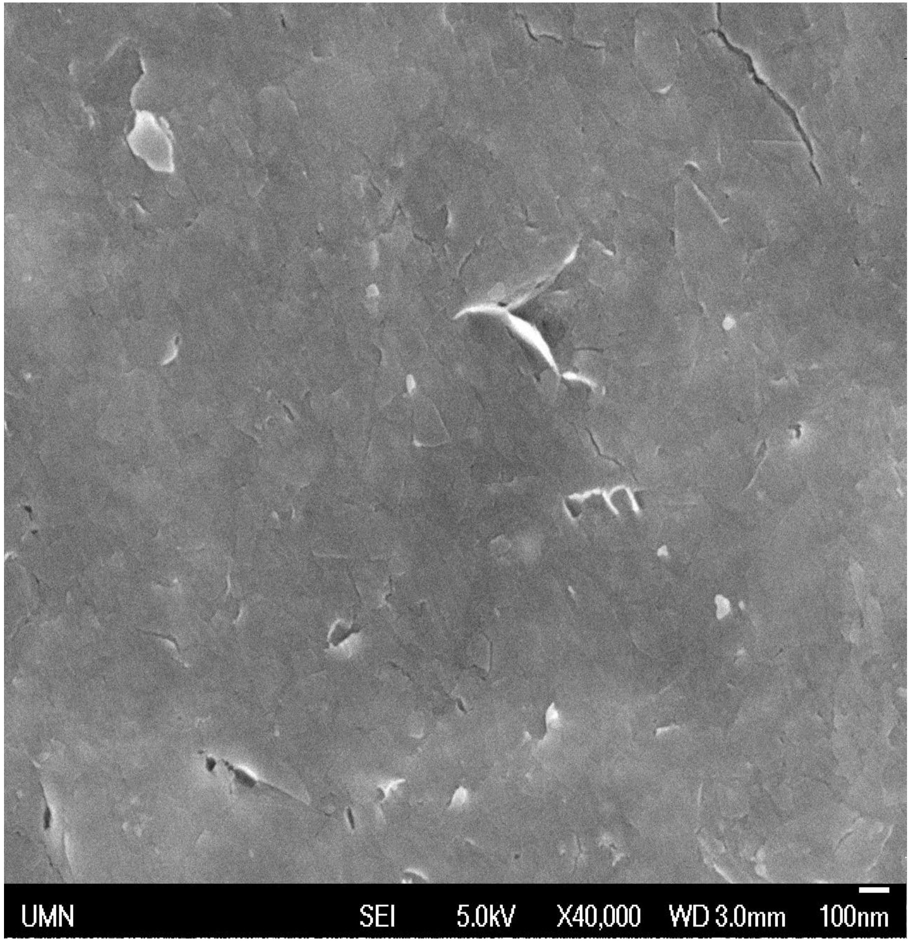
Increase throughput without decreasing selectivity

Membrane Preparation Procedure

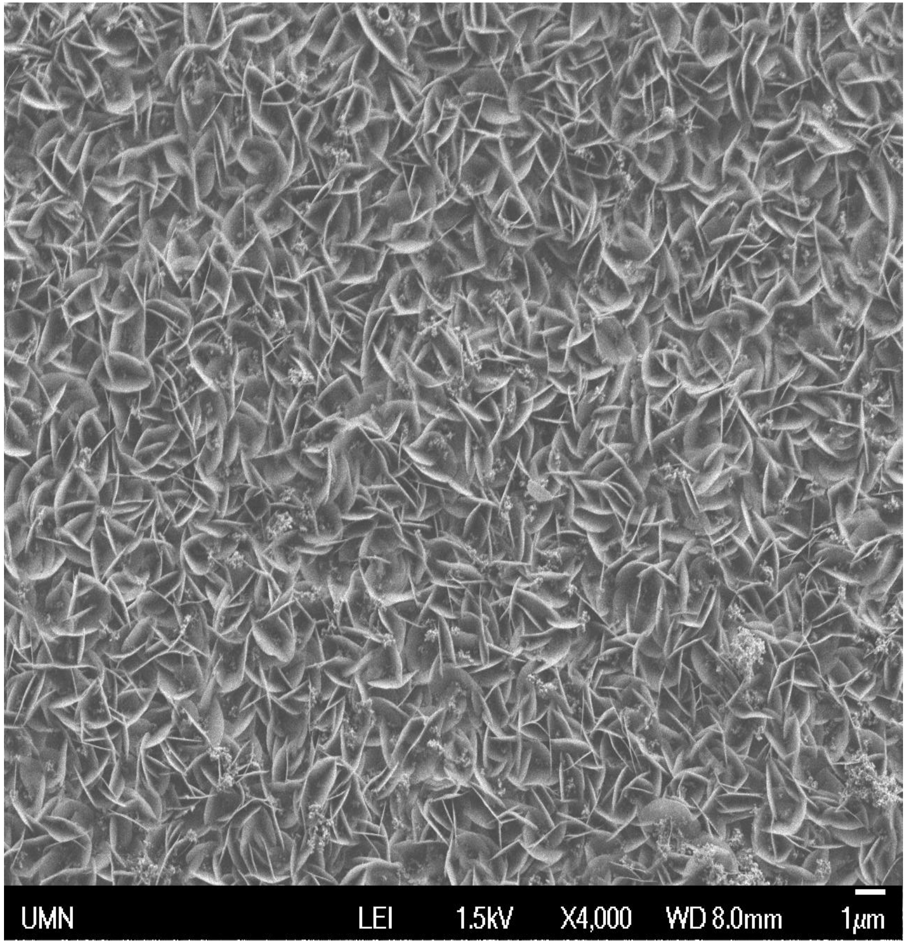


Purified nanosheets in toluene were filtered through porous alumina supports and then secondary growth was conducted.

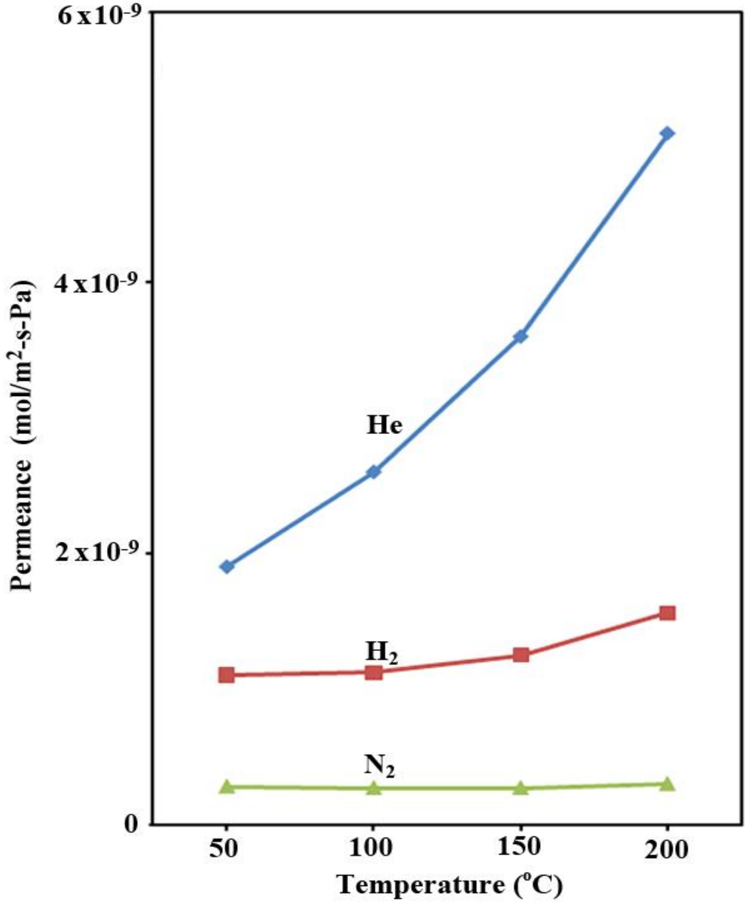
- Exfoliated ITQ-1 on Alumina Disk

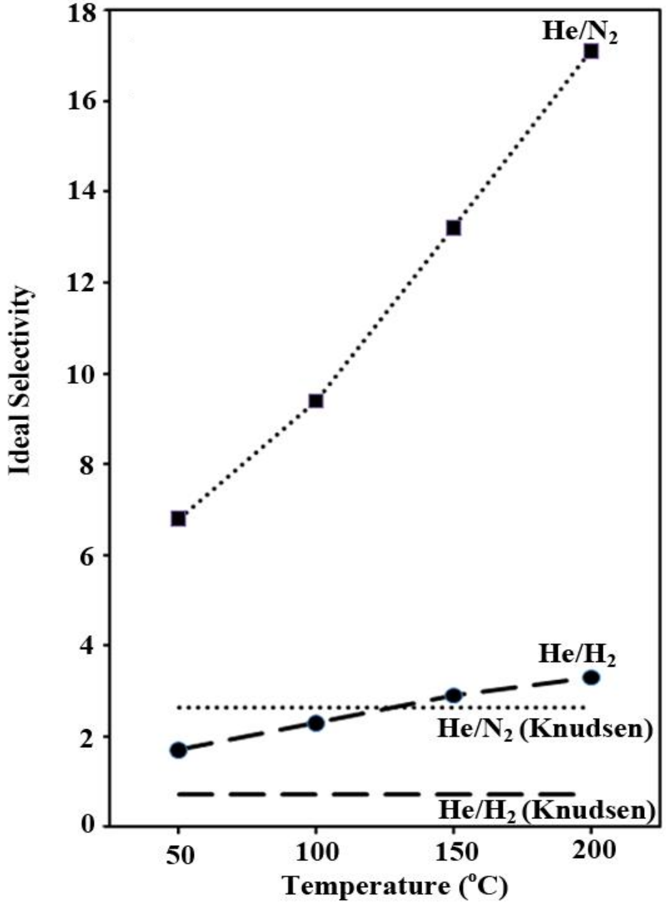


- After Secondary Growth of ITQ-1



Performance of ITQ-1 Membrane





(To be published)

Summary of Experimental Achievement & Future Work

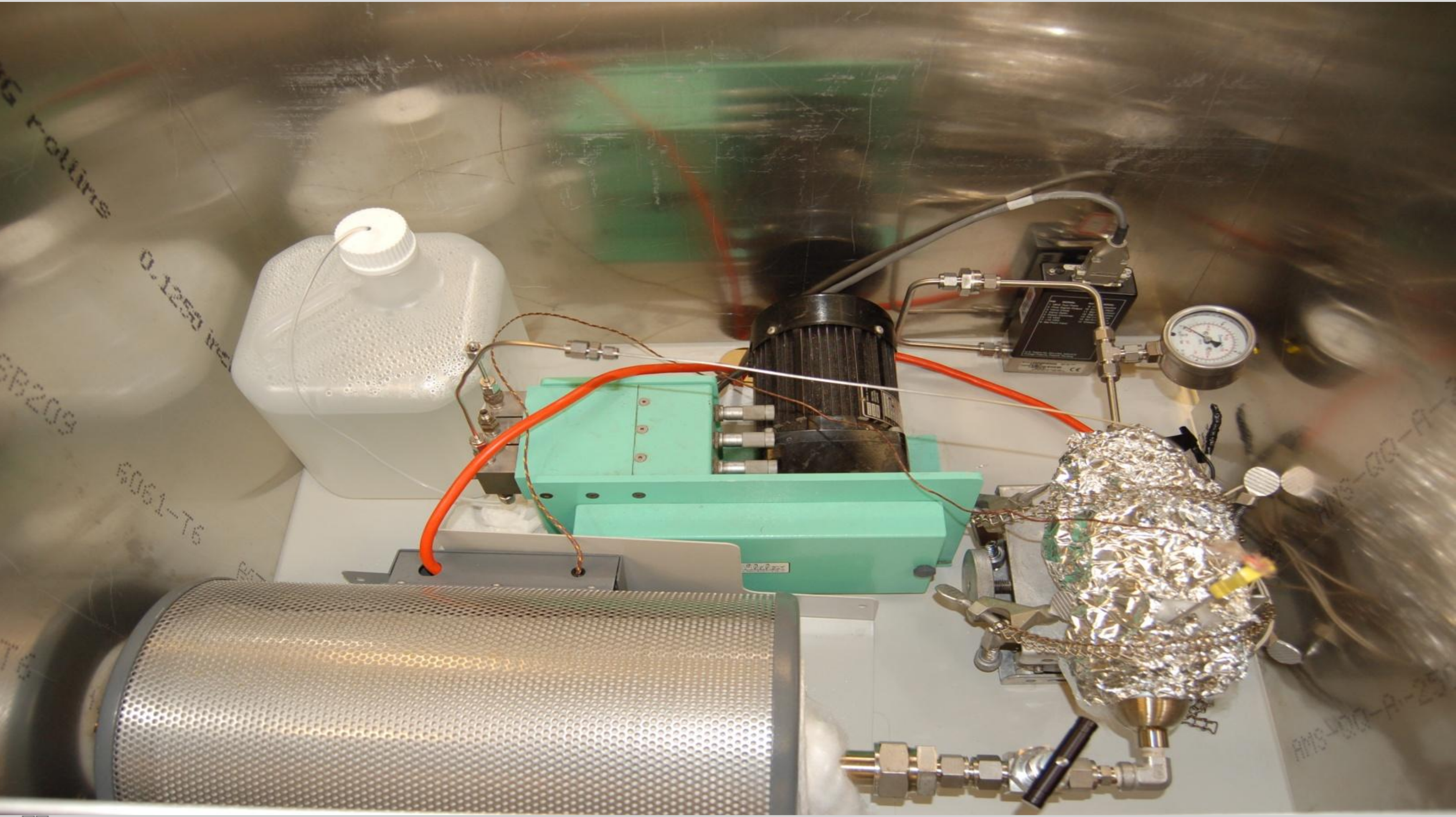
- **Achievement**
  - **prepared hydrogen permselective ITQ-1 membranes using exfoliated MWW structure**

- **Future Work**
  - **working towards meeting proposed target for H_2/CO_2 selectivity**
  - **developing ITQ-1 membranes on tubular supports and investigating their performance at higher temperatures**

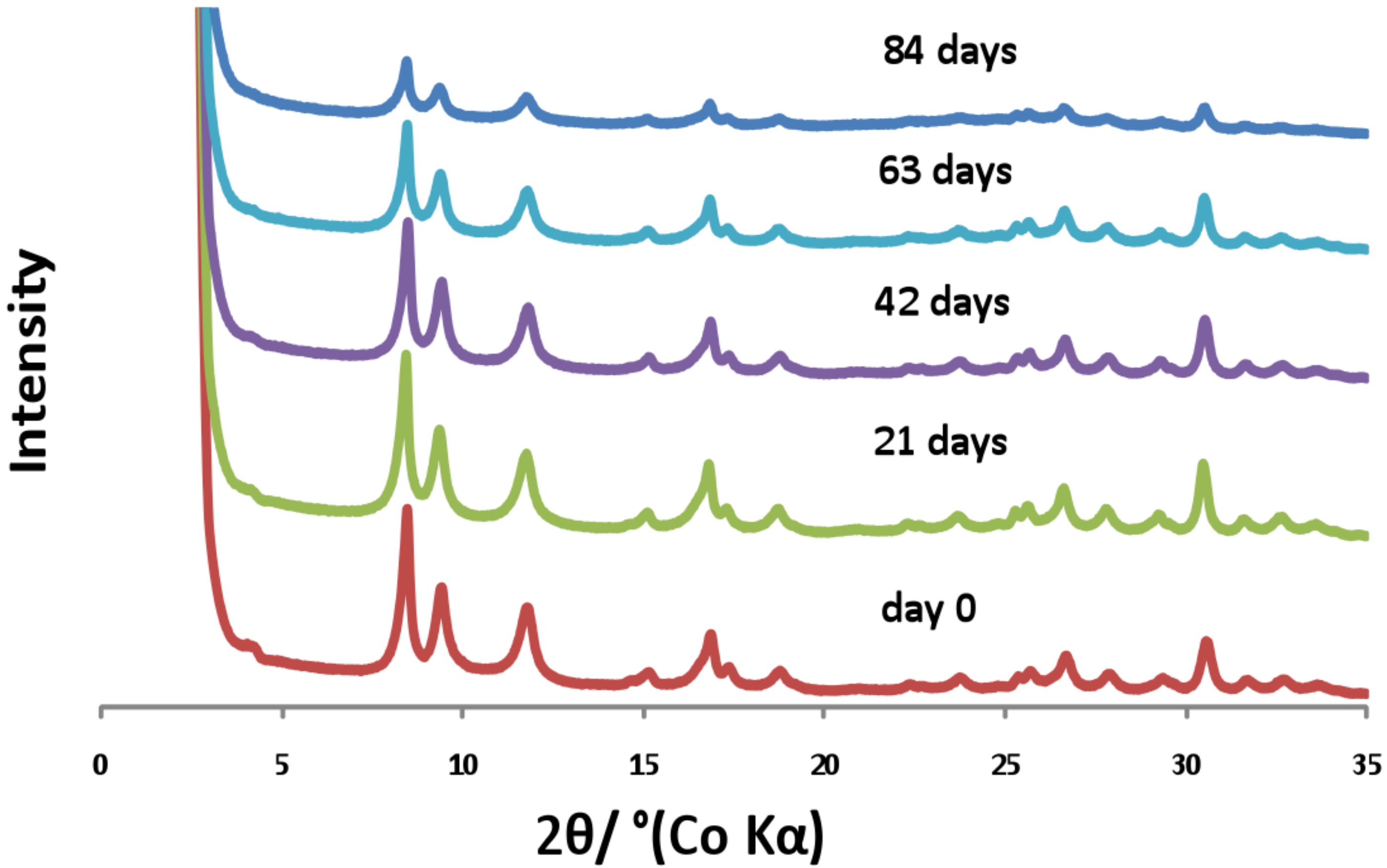
Hydrothermal Treatment Conditions

- **Temperature: 350^{o}C**
- **Pressure: 10 bar (95% steam, 5% nitrogen)**
- **Samples were analyzed in 21 days intervals**

Hydrothermal Stability Setup



Hydrothermal Stability (~95% steam in nitrogen) at 350ºC,10 bar



Summary of Stability Analysis & Future Work

- **Achievement**
  - **developed material showing high hydrothermal stability**

- **Future Work**
  - **performing hydrothermal stability studies on other layered zeolites**

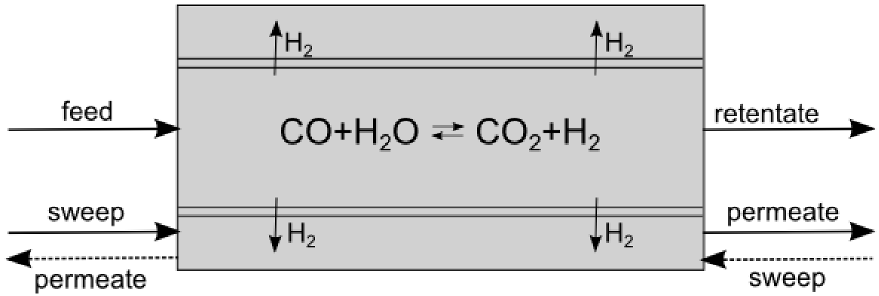
Membrane Reactor Modeling: Objectives and Approach

- **Develop a WGS membrane reactor (MR) model**
  - **perform simulation and optimization studies**
  - **analyze the effect of reactor design on performance**
  - **integrate model in IGCC unit**
- **Determine the membrane characteristics necessary to**
  - **achieve DOE R&D target goal of 90% CO_2 capture [(1),(2)]**
  - **obtain desired H_2 recovery value of 95% [(1)]**
- **Satisfy transportation safety constraints of CO_2 capture stream [(1)]**
  - **low CO concentration obtained by reaching desired CO conversion value of 98%**
  - **H_2 molar fraction below flammability limit of 2%**
- **Minimize membrane cost as a function of surface area required**
- **Received input from DOE/NETL personnel (Drs. John Marano and Jared Ciferno)**

(1) Marano, **Report to DOE/NETL** (2010)
(2) Marano and Ciferno, **Energy Procedia** 1, 361-368 (2009)

MR Modeling Assumptions and Simulation Set Up

Composition (1):
CO = 24.43 %
H_2O = 48.86 %
CO_2 = 5.68 %
H_2 = 19.33 %

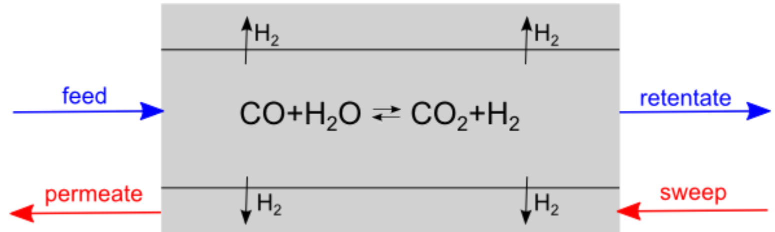


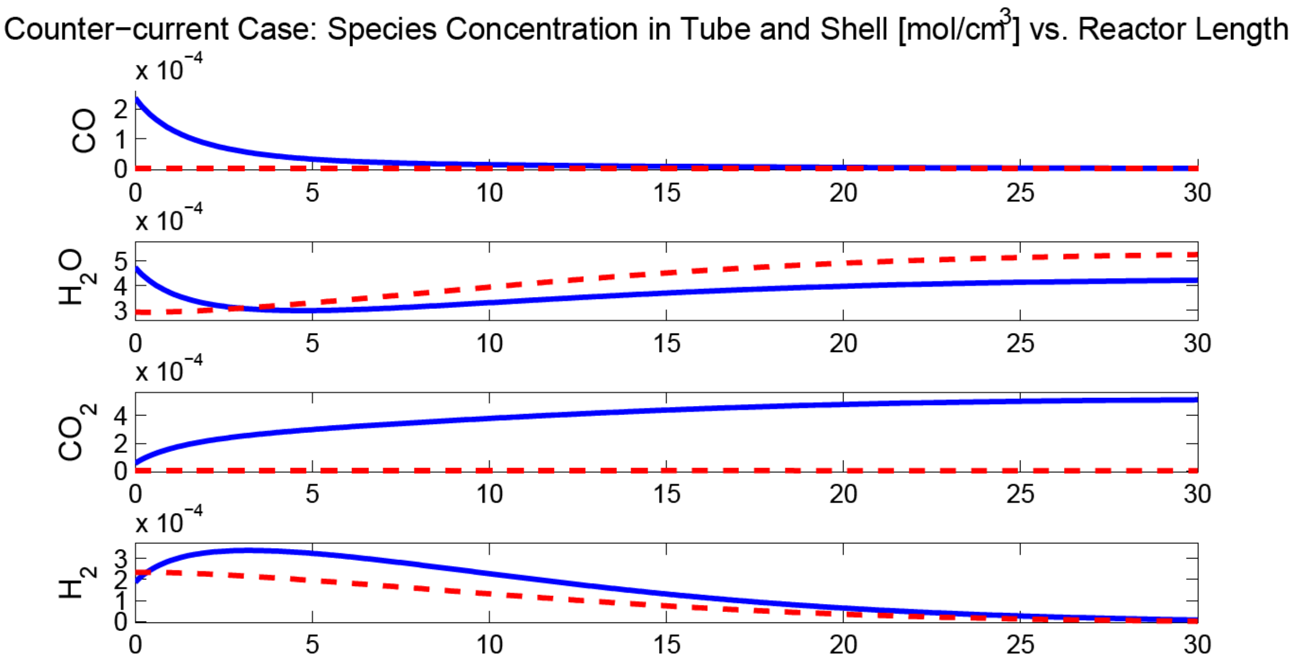
- **Assumptions**
  - **1-dimensional shell and tube reactor**
  - **catalyst packed in the tube side**
  - **thin membrane layer placed on surface of tube wall**
  - **sweep gas flows in the shell side**
  - **plug-flow operation for both shell and tube**
  - **constant temperature and pressure**
  - **steady-state operation**
  - **ideal gas law**

- **Flow configurations**
  - **co-current**
  - **counter-current**
- **Simulation conditions from literature**
  - **catalyst type and reaction rate (2)**
  - **reactor dimensions (3)**
  - **conditions consistent with IGCC specifications**
- **Developed model validated using published simulation data (4)**

(1) Marano, **Report to DOE/NETL** (2010)
(2) Choi and Stenger, **J. Power Sources** 124, 432-439 (2003)
(3) Amelio et al., **Energy Convers. Mgmt** 48, 2680-2693 (2007)
(4) Boutikos and Nikolakis, **J. Membr. Sci.** 350, 378-386 (2010)

Counter-current Simulation Results: Concentration Profiles

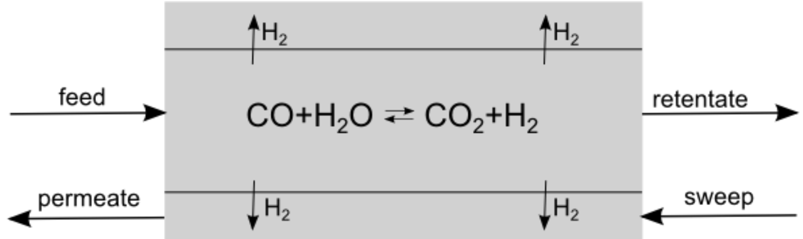




Simulation conditions

- MR length of 30 cm
- Q_{H2} = 0.1 mol/(s.m^2.atm)
- $S_{H2/all}$ = 1000
- steam as sweep gas

Counter-current Simulation Results: Changing Membrane Selectivity



Membrane Reactor Parameter	Value [%] ($S_{H2/all}$ = 1000)	Value [%] ($S_{H2/all}$ = 100)	Value [%] ($S_{H2/all}$ = 10)	Target [%]
$X_{CO} = \frac{\text{CO converted}}{\text{CO in feed}}$	99.84	99.34	**95.02**	**98**
$R_{H_2} = \frac{H_2 \text{ in permeate}}{H_2+CO \text{ in feed}}$	99.06	99.00	97.21	**95**
$C_{CO_2} = \frac{CO+CO_2 \text{ in retentate}}{CO+CO_2 \text{ in feed}}$	98.97	90.15	**29.07**	**90**
$P_{CO_2+H_2O,R} = \frac{CO_2+H_2O \text{ in retentate}}{\text{total in retentate}}$	96.31	96.62	98.30	**95**
$P_{H_2,P} = \frac{H_2 \text{ in permeate}}{\text{total in permeate}}$	44.27	**43.14**	**34.05**	**44**
$y_{H_2,R} = \frac{H_2 \text{ in retentate}}{\text{total in retentate}}$	0.66	0.51	0.01	**(≤)2**

Membrane Reactor Optimization: Problem Formulation

- **Typical WGS reactor design alternatives [(1),(2)]**
  - **pre-shift, membrane separator, WGS reactor**
  - **pre-shift, WGS membrane reactor**
  - **WGS reactor, membrane separator**
  - **stand-alone WGS membrane reactor**
- **Address all alternatives in one formulation**
- **Optimization problem statement [(3)]**

$$\min_{l_1, l_2, l_3, l_4, l_5} \left[cost_m - credit_{H_2} \right]$$

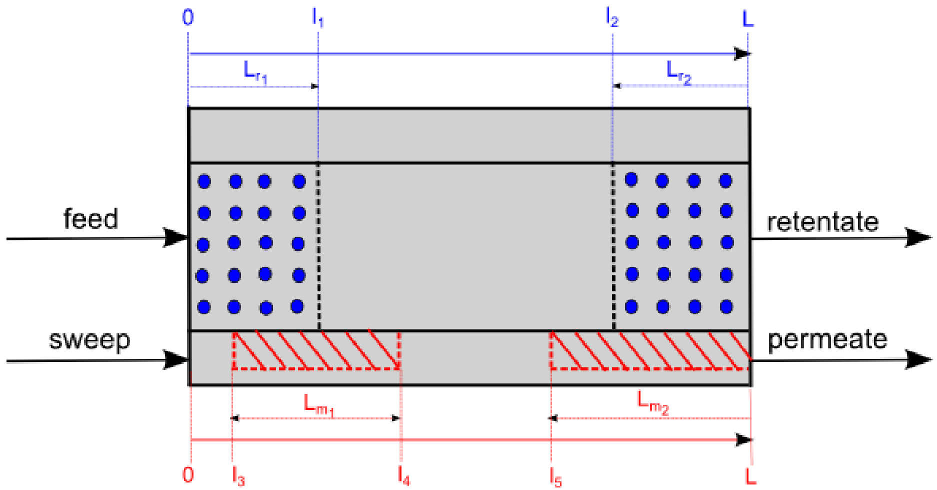
s.t.: target specifications and constraints

in which

$$cost_m = f\left(A_m\right)$$

$$credit_{H_2} = f\left(R_{H_2}\right)$$

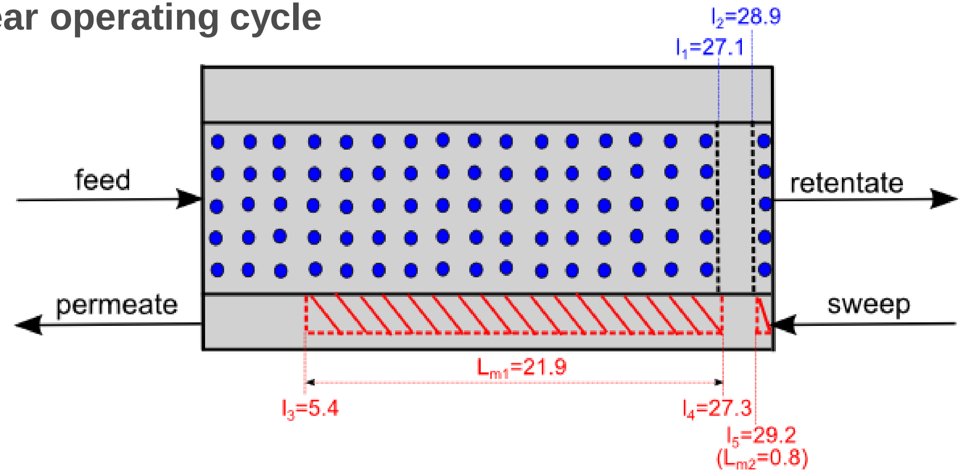
Parameter	Price [$]
zeolite membrane	1,000 - 10,000/m^2
H_2 fuel	1.78/kg



(1) Marano and Ciferno, **Energy Procedia** 1, 361-368 (2009)
(2) Bracht et al., **Energy Convers. Mgmt** 38, S159-164 (1997)
(3) Lima et al., **In preparation** (2011)

Membrane Reactor Optimization: Results

- Benchmark for study: improve successful counter-current case
- Problem initial guess: MR configuration
- Solution for 1 year operating cycle



- Length of membrane layer: $L_{m1} + L_{m2} = 22.7$ cm
- Solution indicates
  - optimal design: short pre-shift reactor followed by long MR
  - potential savings in membrane material (≈ 25%)
    - large-scale [1] ($A_m \approx 2000\ m^2$) $\Rightarrow$ savings as high as $5,000,000

(1) Bracht et al., **Energy Convers. Mgmt** 38, S159-164 (1997)

Modeling Conclusions & Future Work

- **Conclusions**
  - **MR model developed for simulation and optimization studies**
  - **simulation results indicated successful counter-current cases**
  - **optimization formulation guided selection of optimal reactor design for WGS reaction**
- **Future Work**
  - **perform preliminary cost analysis using MR model**
  - **develop IGCC system model**
    - **first step: Matlab model of separate units (gasifier, ASU, turbines, and heat exchangers)**
    - **simplified gasifier model developed assuming Conoco-Phillips design [1]**
    - **integrate units (including MR) in IGCC plant (Matlab and Aspen simulations)**

(1) Jillson et al., **J. Proc. Cont.** 19, 1470-1485 (2009)